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## (54) A METHOD OF EXTRACTION OF NICKEL AND OF COPPER CONTAINED IN OCEAN-FLOOR MANGANIFEROUS ORE MODULES

(71) We, COMISSARIAT A  
L'ÉNERGIE ATOMIQUE, a French Body  
Corporate, of 29, rue de la Fédération, Paris  
15e, France, do hereby declare the  
invention, for which we pray that a patent  
may be granted to us, and the method by  
which it is to be performed, to be  
particularly described in and by the  
following statement:—

This invention relates to a method of  
extraction of nickel and of copper  
contained in ores of the type constituted by  
the manganiferous nodules found on the  
ocean floor.

The nodules formed in the ocean floor  
are known as manganese or manganiferous  
nodules since their main constituent is  
MnO<sub>2</sub>. The appearance of these nodules  
and the mean concentration of metals  
therein, related to the ocean zones in which  
they occur, have been described in detail by  
J. L. Mero, in particular in United States  
patent No. 3,169,856 which gives a list of the  
principal metals contained in the nodules  
and their concentrations.

The following composition, of weight  
percentage of metals in manganese nodules,  
can be given by way of example:

Mn	8	to 40	%
Fe	3	to 25	%
Al	0.5	to 3	%
Ni	0.7	to 2	%
Cu	0.5	to 1.6	%
Co	0.1	to 0.5	%
Zn	0.05	to 0.12	%
Ce	0.1	%	
Mo	0.03	to 0.1	%
La	0.026	%	
Ga	0.001	to 0.023	%
Nd	0.022	%	
Sn	0.008	to 0.01	%
Cr	0.007	to 0.01	%
Sm	0.005	%	
Cd	0.0005	%	

K	0.7	to 3	%	45
Na	1	to 3	%	
Mg	0.5	to 2.8	%	
Ca	0.8	to 3	%	
SiO <sub>2</sub>	12	to 20	%	

The recovery of nodules by dredging,  
injection of air or hydraulic pumping is  
being studied and has formed the subject of  
a large number of patents among which can  
be cited United States patents Nos:  
3,226,854, 3,456,371, 3,480,326, 3,504,943,  
Canadian patents Nos: 928,337 and 928,338  
and French patent No 2,067,797.

Among the recoverable metals, nickel  
and copper offer the most attractive  
prospects since world reserves of nickel and  
copper are decreasing rapidly and it is  
becoming advantageous to process low-  
grade ores. Cobalt, zinc, gallium, tin, the  
rare earths are contained in nodules at  
concentrations such that the recovery of  
these metals can have the effect of  
increasing the commercial value of the ore  
if the recovery operation is not a costly one.  
The metal value of iron is of no interest on  
account of its low concentration and the  
many impurities which are also present.  
Manganese, which is the main constituent  
of nodules, is not strictly speaking a non-  
recoverable metal. But the exploitation of  
nodules is contemplated with a view to  
making up for depleted resources of nickel  
and copper; so far as these two metals are  
concerned, the market requirements would  
actually lead to overproduction of  
manganese if all the manganese contained  
in nodules were recovered. It is for this  
reason that a simple and inexpensive  
process which makes it possible to separate  
nickel and copper, as well as a proportion of  
other metals contained in nodules, while  
leaving the iron in the steriles becomes  
particularly attractive if such a process  
makes it possible at the same time to

recover the desired quantity of manganese progressively as markets develop.

Processing of nodules is usually carried out by three different methods. In accordance with a first method described in French patents Nos: 2,098,453, 2,098,454, 2,098,455, 2,113,978 and the German patent Application No DOS 2,135,731, a reduction is carried out and this is followed by leaching with ammonia. In accordance with a second method described in French patent No 2,090,301, treatment is carried out with hydrochloric acid and with steam. In accordance with a third method described in French patent No 2,090,300, United States patent No 3,169,856 and the German patent Application No DAS 2,150,785, a treatment is carried out with sulphurous anhydride in an aqueous medium.

These methods suffer from a disadvantage in that they entail the use of costly apparatus so far as the first two methods are concerned or that they result in total recovery of the manganese in the case of the last two methods mentioned.

In accordance with the invention, these disadvantages have now been successfully overcome, or at least mitigated, by adopting a method which permits recovery of copper and nickel while making it possible to control the production of manganese at will.

According to the present invention there is provided a method of extraction of metal from manganiferous ore nodules, which comprises neutralizing (as hereinafter defined) by attack of crushed ore using water and sulphuric acid, introduction of a controlled quantity of sulphur dioxide gas corresponding to the stoichiometry of the reaction of sulphation of manganese dioxide by sulphur dioxide at pH in the range of from 1.5 to 4 with agitation in order to break down the ore structure and promote subsequent dissolution of the metals, comprising nickel, copper and the desired quantity of manganese, leaching of the ore with sulphuric acid at a pH value within the range of 1 to 3 in order to selectively dissolve the nickel and the copper, and separating the solid and liquid phases. Advantageously, there is provided a method of extraction of metal from ocean floor manganiferous ore nodules, which method comprises the steps of:

- a) crushing of the ore;
- b) neutralization (as hereinafter defined) of crushed ore by means of aqueous sulphuric acid;
- c) introduction of a controlled quantity of sulphur dioxide gas corresponding to the stoichiometry of the reaction of sulphation of manganese dioxide by sulphur dioxide at

a pH value within the range of 1.5 to 4 with agitation in order to break down the ore structure and promote subsequent dissolution of the metals, comprising nickel, copper and the desired quantity of manganese;

d) leaching of the ore with sulphuric acid at a pH value within the range of 1 to 3 selectively to dissolve the nickel and the copper;

e) separation of the solid and liquid phases;

f) separation of the metals contained in the liquid phase.

The injection at a predetermined pH value of very small quantities of sulphur dioxide into the solution forming a pulp with the ore has the effect of accelerating the desorption of the nickel and the copper, and of appreciably improving the recovery of these metals without increasing the rate of dissolution either of iron or of manganese if so desired. Should it be found necessary to solubilize larger quantities of manganese, it is only necessary to increase the time of injection of  $\text{SO}_2$  (thereby increasing the amount of  $\text{SO}_2$  injected) in order to produce larger quantities of manganese. When this injection has been carried out, desorption of the nickel and the copper can be completed by continuing the process of leaching with sulphuric acid.

The method under consideration has been applied in accordance with the main steps which are illustrated schematically in the accompanying figure, by way of example.

The nodules containing manganese, iron, copper, nickel, cobalt, zinc and other metals such as previously listed were first crushed to a particle size below 160 microns corresponding to a screen size of 23-mesh but this value is not given by way of limitation and the method is equally applicable to particle sizes corresponding to 20 to 45-mesh screens (French scale — equivalent to about 80 microns to 1,000 microns). The crushed ore was then mixed with fresh water or sea water acidulated with sulphuric acid having a pH value of about 2 so as to form a pulp containing up to 50% of solids. The quantity of ore contained in this pulp is not an essential point but must be such that the mixture behaves as a fluid. The pH value of the solution which has risen to approximately 6 in contact with the ore was restored to between 4 and 2 by sulphuric acid. This operation which does not give rise to any solubilization of metals is herein referred to as ore neutralization. At this time, a predetermined quantity of sulphur dioxide was injected into the pulp by percolation for example, while maintaining regular

agitation of the pulp. The  $\text{SO}_2$  makes it possible to break down the surface structure of the manganese lattices and to open the pores in order to facilitate subsequent diffusion of the metal ions. Moreover, the  $\text{SO}_2$  causes practically instantaneous dissolution of from 3 to 15% of the nickel or even more, part of the cobalt and from 1 to 10% of the manganese or even more, depending on the quantity of sulphurdioxide injected. This quantity which determines the rate of recovery of manganese can be calculated by taking account of the stoichiometry of the reaction of sulphation of manganese dioxide by the sulphurdioxide.

The progressive variation of the pH value, however, also serves to provide indications as to how the extraction is proceeding since the pH value in fact rises by one-tenth of a unit each time 3 to 4% of the manganese is dissolved.

After injection of  $\text{SO}_2$ , leaching of the nodules is effected with sulphuric acid at a controlled pH in the range of pH 1 to 3. Dissolving of the nickel and the copper then proceeds rapidly, thus attaining in about 6 hours the yields obtained in about 60 hours by mere sulphuric acid leaching on the same ore and under the same conditions. Moreover, when the leaching process was continued, the limit of the yields obtained exceeded by 10 to 20% the limit of the yields obtained by mere sulphuric acid leaching.

After the leaching process, the solution containing nickel, copper, manganese and other metals was separated from the solid residue (known as steriles). The steriles were washed and could then be subjected to

conventional metallurgical processing when it was desired to recover the fraction of cobalt which had remained in the steriles. This method of leaching can be performed in countercurrent operation, continuous operation or batchwise.

It has been observed that the kinetics of dissolution of the metals depended on the temperature, the pressure, the agitation of the pulp and the pH value of leaching with  $\text{H}_2\text{SO}_4$ , but such variables are neither critical nor essential.

The following Examples further illustrate the present invention. Herein, all percentages being by weight unless otherwise specified.

#### EXAMPLE 1.

Influence of sulphur dioxide on the sulphuric acid leaching process

By following the general method outlined above, 100 g of manganese nodules were attacked at  $60^\circ\text{C}$  after crushing to  $160\mu$  and forming into a pulp with 300 g of water. The composition of the nodules was as follows: Mn 21.5%, Fe 6.8%, Ni 0.97%, Cu 0.70%, Co 0.20%,  $\text{H}_2\text{O}$  13.8% (at  $110^\circ\text{C}$ ). These percentages are expressed by weight with respect to dry material.

The injection of about 0.5 liter of  $\text{SO}_2$  was carried out at a pH of 3 and the pH was increased to pH 3.2. Sulphuric acid leaching was performed at a pH of 1.5. Table 1 below gives the dissolution kinetics obtained. By way of comparison, this table also records the dissolution kinetics obtained under the same conditions of temperature, pulp consistency, particle size, and pH with no  $\text{SO}_2$  treatment prior to sulphuric acid leaching.

TABLE 1

	Dissolution yield Leaching with SO <sub>2</sub> +H <sub>2</sub> SO <sub>4</sub>				
	Mn	Fe	Ni	Cu	Co
After neutralization of ores	1	0	1	1	0
After injection of SO <sub>2</sub>	4.3	0	9	2	1
After 2 hrs of leaching	4.7	0.7	29	32	0.6
After 6 hrs of leaching	5.1	3.5	54	52	1
After 12 hrs of leaching	5.4	3.3	60	57	1.3
	Mere sulphuric acid leaching				
Leaching time:					
After 3 hours	—	—	32	25	—
After 6 hours	—	—	36	26	—
After 12 hours	—	—	44	32	—
After 24 hours	—	—	—	—	—
After 48 hours	1	1	49	34	—
After 100 hours	1	1	63	40	0.7

It is apparent from this table that the use of SO<sub>2</sub> prior to leaching with sulphuric acid permits a considerable acceleration of the dissolution kinetics.

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## EXAMPLE 2.

Influence of the pH value when sulphur dioxide is injected

Leaching operations were carried out over periods of 6 hours on the same batch of nodules and under the same conditions as in Example 1 by varying, in the case of each leaching operation, the pH value at the beginning of injection of 0.5 liter of sulphur dioxide.

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TABLE 2

pH at start of injection	pH after injection	% Dissolution yield				
		Mn	Fe	Ni	Cu	Co
6.2	5	12.2	5.6	64	67.5	2.5
4	4	9	3.5	60	62	2.5
3	3.2	8	3.6	65	61	1.7
2	2.3	11	4	58	58	2.5
1.5	1.5	11	6	64	67	3

These results show that the preferred pH values are within the range of 1.5 to 4.

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In fact, at the most basic pH values, manganese dissolves more readily than nickel at the time of injection of SO<sub>2</sub>. At a pH of 5.5, 9% of manganese is dissolved as compared with 4% of nickel and more of the copper whereas 4% of manganese dissolves

at a pH value of 3 as compared with 9% of nickel.

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At the more acid pH values, dissolutions of nickel and of copper are highly facilitated (30% nickel, 25% copper and 9% manganese are dissolved after injection of SO<sub>2</sub> at a pH value of 2) but these dissolutions are accompanied by the

30



dissolution of part of the iron when the percentage of manganese recovered is increased.

### EXAMPLE 3.

- 5 Influence of the quantity of sulphur dioxide injected

Under conditions which are identical to

those of the preceding examples, nodules were attacked with increasing quantities of  $\text{SO}_2$  at a pH value of 3; after sulphuric acid leaching at a pH of 1.5, the dissolution yields of the metals were as follows: 10

TABLE 3

Quantity of $\text{SO}_2$ injected in 300 g of water	pH after injection	% dissolved after injection of $\text{SO}_2$					% dissolved after leaching (12 hours)				
		Mn	Fe	Ni	Cu	Co	Mn	Fe	Ni	Cu	Co
0.25 l	3.1	1.2	0	3	4	0	2.8	3	61	47	<1
0.5 l	3.2	4.3	0	9	4	<1	8.3	4	73	62	1.2
0.75 l	3.4	10	0	15	2.5	1	14	3	75	62	1.6
1 liter	4.0	28	0	25.9	1.8	13			87	90.5	12.4
3 liters		72	0	72	0.1	64					

- 15 The dissolution percentage ratio of manganese is therefore directly related to the quantity of  $\text{SO}_2$  injected and the increase in the pH value is an indication which makes it possible to control the percentage of manganese dissolved.
- 20 Dissolution of the cobalt is also promoted by dissolution of the manganese.

### EXAMPLE 4.

Influence of the pH of the sulphuric acid leaching process

In the general method outlined above, by injecting 0.5 liter of sulphur dioxide per 100 g of nodules having a pH value of 3 and by then leaching the nodules at a pH value of 1.5 or 2 for a period of 12 hours, the following results were obtained: 25 30

TABLE 4

	Dissolution Yield			
	Mn	Fe	Ni	Cu
Leaching at pH 1.5	8.2	3.5	65	60
Leaching at pH 2	7.8	0.1	60	45

Leaching at a less acid pH therefore makes it possible to obtain excellent selectivity for iron.

### EXAMPLE 5.

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Influence of temperature

In the general method outlined above,

injection of 0.5 liter of  $\text{SO}_2$  per 100 g of nodules was followed by leaching with  $\text{H}_2\text{SO}_4$  at a pH value of 1.5 for a period of 6 hours. 40

TABLE 5

Leaching T°C	Dissolution Yield				
	Mn	Fe	Ni	Cu	Co
35°	8	2.6	30	47	0.7
60°	8	3.5	60	56	1.5
90°	7.2	3.3	66	54	3

A moderate increase in the leaching temperature therefore makes it possible to accelerate the dissolution of Fe, Ni, Cu and Co. injection of 0.5 liter of SO<sub>2</sub> per 100 g of nodules at a pH of 3 was followed by; sulphuric acid leaching at a pH of 1.5 for 12 hours. 10

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## EXAMPLE 6.

Influence of particle size

In the general method outlined above

TABLE 6

Particle size	Dissolution Yield				
	Mn	Fe	Ni	Cu	Co
<63 $\mu$	9	3.5	74	58	0
63-180 $\mu$	8.3	4	73	62	1.2

Very fine particle sizes are thus not necessary for good performance of the method of the present invention. 15

## EXAMPLE 7.

Influence of the injection of air with sulphur dioxide gas

In the general method outlined above, injection of 0.5 l of SO<sub>2</sub> per 100 g of nodules at a pH of 3; was followed by sulphuric acid leaching at a pH of 1.5 for 6 hours. 20

TABLE 7

	Dissolution Yield				
	Mn	Fe	Ni	Cu	Co
without air	8	3.6	65	61	1.7
with air	8.9	2.6	64	61	2

The air which is injected with SO<sub>2</sub> does not nullify the attack, results in enhanced selectivity of leaching with respect to iron and can be employed without difficulty for the agitation of the pulp. 25

## EXAMPLE 8.

Influence of the pH, of the sulphur dioxide gas and of the leaching time 30  
Two tests performed in several stages

under conditions which were identical with those of Example 1 and with sulphuric acid leachings at a pH of 1.5 or 2 and different quantities of injected sulphur dioxide produced the results indicated in Table 8 hereunder. 35

TABLE 8

Leaching pH		1.5			2	
Quantity of SO <sub>2</sub> injected per 100 g of nodules		0.5 liter			0.5 liter	
Stages		1	2	3	1	2
Dissolution yield	Mn	8.3	9.1	10.7	7.9	8.5
	Fe	3.3	5	7.3	<1	0.5
	Ni	60	80	84.5	61	66.3
	Cu	57	69	76	40	47.2
	Co	1.3	2.5	3.3	1	1.2

Leaching pH		1.5				1.5			
Quantity of SO <sub>2</sub> injected per 100 g of nodules		0.25 liter				0.75 liter			
Stages		1	2	3	4	1	2	3	4
Dissolution Yield	Mn	2	2.7	3.2	3.5	14	15.6	16.3	16.7
	Fe	2.2	2.4	3.5	4.1	3	3.8	4.8	5.7
	Ni	53	64	65	71.4	75	81.6	85	88
	Cu	43.8	54	61.6	65.5	62	69.2	74	77
	Co	0.7	0.9	1.2	1.4	1.6	2	2.4	2.5

1st stage: 12 hours of leaching

2nd stage: 6 hours of leaching

3rd stage: 6 hours of leaching

4th stage: 6 hours of leaching

5 This method has therefore made it possible to recover in 24 to 30 hours the greater part of the nickel and the copper and the desired quantity of manganese by carrying out extremely simple leaching operations while using only a very small quantity of reagents of the order of 180 kg of H<sub>2</sub>SO<sub>4</sub> per metric ton of nodules.

10 It should be pointed out that this method permits an alternative possibility of isolating part of the copper alone at the outset of the sulphuric acid leaching process. Extraction

of the copper from the leach solution by a cation exchanger (of the "Lix" or "Kelex" type) accordingly makes it possible to regenerate sulphuric acid which can then be employed for neutralization of the ore. It is therefore possible by this means to reduce the consumption of acid.

The first stage of the leaching process was performed at a pH of 1.5 with an injection of 0.5 l of SO<sub>2</sub> at a pH of 3. By bringing the temperature to 35°C, preferential dissolving of the copper was thus made possible.

TABLE 9

	Mn	Fe	Ni	Cu	Co
Percentage of metal dissolved after 3 hours of leaching	6.8	1.5	19	41	0.7

30 After attack and liquid-solid separation, the sulphuric acid solutions to be treated had a pH of 1.5 to 2 and the following compositions:

	Fe <sup>III</sup>	~ 0.4 g/l
	Ga	~ 0.003 g/l
	Al	~ 5 g/l
35	Cu	~ 3.2 g/l
	Zn	~ 0.13 g/l
	Ni	~ 4 g/l
	Co	~ 0.02 to 0.5 g/l
	Mn	~ 6.6 to 50 g/l
40	Ce	~ 0.206 g/l
	La	~ 0.07 g/l
	Nd	~ 0.07 g/l
	K	~ 2.1 g/l
	Mg	~ 6 g/l
	Na	~ 6 g/l

45 Separation of the other metals, which is not essential to the present invention, was carried out as follows:

The copper was extracted selectively by a cation exchanger of the "Lix" or "Kelex" type diluted in kerosene with heptanol or isodecanol as additive. The copper was stripped by means of the solution of copper sulphate and sulphuric acid derived from the electrolysis of copper in sulphuric acid.

55 Iron, gallium, aluminum and traces of chromium were then precipitated from the stripped solution with lime between 50° and 60°C and at a pH of 3.3. The precipitate was then reduced to pulp by employing sulphuric acid at a pH of 4 in order to redissolve any nickel and cobalt which may have been hydrolyzed in contact with the particles of lime.

The solution contained alkali metals and alkaline-earth metals, nickel, cobalt, manganese and a certain number of impurities constituted by unprecipitated traces of iron, gallium and aluminum, zinc, cerium, lanthanum and neodymium. These metals were all coextracted in a single stage. The aqueous solution having a pH of 4 was contacted with a solvent consisting of 20% D 2 EHPA—5% TBP—75% SOLVESSO, although the nature of the solvents employed does not have any limitative character. Control of the pH value was ensured by employing D 2 EHPA, mostly as the sodium salt. When the exit pH value of the aqueous phase was equal to 3, the iron, aluminum, zinc and rare earths were precipitated but this was not the case with the nickel, the cobalt and the manganese. In the case of small increases in pH, the manganese which was extracted prior to the nickel and the cobalt saturated the solvent and this made it possible to avoid any loss of nickel and cobalt.

All these metals with the exception of iron were then stripped with 1.5 N sulphuric acid. The iron which was stripped in a basic medium at the same time as D 2 EHPA was converted back to sodium salt and it was possible to maintain the iron in solution by means of complexing agents.

After this extraction cycle, the pH of the aqueous solution containing nickel, cobalt, manganese and the alkali metals and alkaline-earth metals was brought to a value between 3.5 and 4.

The cobalt was then extracted by a mixture of an extraction agent having a base of oxime and of a carboxylic acid. Mixtures of this type in fact make it possible to increase the extraction kinetics of cobalt to an appreciable extent and to permit stripping of this latter in a dilute acid medium as well as to achieve a considerable reduction in the kinetics of extraction of the nickel which accordingly remains in the raffinate. By way of example, mixtures of this type can consist of "Lix—63" or 10% "Lix—64 N" or 5% "Kelex—100" mixed with 0.1 M "Versatic" acid or 0.1 M naphthenic acid or  $\alpha$ -bromolauric acid diluted in kerosene or "Solvesso". This operation accordingly makes it possible to purify the nickel by withdrawing the cobalt from the aqueous phase while minimizing nickel losses. The words "Lix" and "Solvesso" are Trade Marks.

The cobalt was stripped with sulphuric acid. The nickel was then extracted by an oxime ("Lix" or "Kelex") having a pH of 4 and stripped with an acid solution.

The manganese alone remained in the raffinate together with the alkali metals and the alkaline-earth metals. The pH of the aqueous phase was brought to the value of

8.5 by means of a basic agent and the manganese was precipitated in the form of  $\text{MnO}_2$  by the oxidizing action of air.

It was possible to treat the liquid effluents in order to recycle the  $\text{SO}_2$  which had been associated with the manganese. To this end, the basic agent employed at the time of precipitation of  $\text{MnO}_2$  was  $\text{MgO}$ . The magnesium sulphate was then roasted in the well-known manner and  $\text{SO}_2$  and  $\text{MgO}$  were regenerated.

#### WHAT WE CLAIM IS:—

1. A method of extraction of metal from manganiferous ore nodules, which comprises neutralizing (as hereinbefore defined) by attack of crushed ore using water and sulphuric acid, introduction of a controlled quantity of sulphur dioxide gas corresponding to the stoichiometry of the reaction of sulphation of manganese dioxide by sulphur dioxide at a pH in the range of from 1.5 to 4 with agitation in order to break down the ore structure and promote subsequent dissolution of the metals, comprising nickel, copper and the desired quantity of manganese, leaching of the ore with sulphuric acid at a pH value within the range of 1 to 3 in order to selectively dissolve the nickel and the copper, and separating the solid and liquid phases.

2. A method of extraction of metal from ocean floor manganiferous ore nodules, which method comprises the steps of:

a) crushing of the ore;

b) neutralization (as hereinbefore defined) of crushed ore by means of aqueous sulphuric acid;

c) introduction of a controlled quantity of sulphur dioxide gas corresponding to the stoichiometry of the reaction of sulphation of manganese dioxide by sulphur dioxide at a pH value within the range of 1.5 to 4 with agitation in order to break down the ore structure and promote subsequent dissolution of the metals, comprising nickel, copper and the desired quantity of manganese;

d) leaching of the ore with sulphuric acid at a pH value within the range of 1 to 3 selectively to dissolve the nickel and the copper;

e) separation of the solid and liquid phases;

f) separation of the metals contained in the liquid phase.

3. A method according to Claim 1 or 2, wherein the neutralization is performed by means of aqueous sulphuric acid having a pH equal to 2 in a quantity which is sufficient to provide a pH corresponding to that required for injection of the sulphur dioxide.

4. A method according to Claim 1, 2 or 3,



wherein the sulphuric acid leaching process is carried out with sulphuric acid having a pH value within the range of 1.5 to 2 at a temperature within the range of 35 to 90°C for a period of 2 to 12 hours.

5 5. A method according to any one of the preceding claims, wherein the solution obtained on completion of step (e) is contacted with a liquid ion exchanger having a base of oxime and of a carboxylic acid in which the copper is retained and then stripped by means of a solution of copper sulphate and sulphuric acid derived from electrolysis of copper.

15 6. A method according to Claim 5, wherein to the copper free liquid discharged from the liquid ion exchanger lime is added between 50 and 60°C to a pH equal to 3.3 to precipitate partially iron, gallium, aluminum, chromium and is then contacted at pH 4 with a solvent constituted by 20% D 2 EHPA, 5% TBP and 75% organic solvent in order to extract the remaining iron and aluminum as well as zinc, rare earths and other metal impurities.

25 7. A method according to Claim 6, wherein the aqueous phase derived from the solvent extraction process is extracted by means of a mixture having an oxime base and of carboxylic acid of the naphthenic type which is loaded with cobalt.

30 8. A method according to Claim 7, wherein the aqueous phase freed from cobalt having a pH value equal to 4 is treated by means of an oxime which extracts the nickel.

35 9. A method according to Claim 8, wherein the aqueous phase freed from nickel having a pH value equal to 8.5 is treated in order to separate the manganese in the form of a precipitate of  $MnO_2$ .

40 10. A method in accordance with Claim 1 and substantially as described in foregoing Example 1.

11. A method in accordance with Claim 1 and substantially as described in foregoing Example 2. 45

12. A method in accordance with Claim 1 and substantially as described in foregoing Example 3. 50

13. A method in accordance with Claim 1 and substantially as described in foregoing Example 4.

14. A method in accordance with Claim 1 and substantially as described in foregoing Example 5. 55

15. A method in accordance with Claim 1 and substantially as described in foregoing Example 6.

16. A method in accordance with Claim 1 and substantially as described in foregoing Example 7. 60

17. A method in accordance with Claim 1 and substantially as described in foregoing Example 8. 65

18. A method in accordance with Claim 1, substantially as hereinbefore described with reference to the accompanying drawing.

19. Metal whenever extracted by the method of any one of the preceding claims. 70

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